PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-185804
(43)Date of publication of application : 09.07.1999

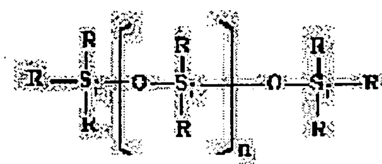
(51)Int.CI. H01M 10/40

(21)Application number : 09-363895
(22)Date of filing : 18.12.1997

(71)Applicant : TOYAMA YAKUHIN KOGYO KK
(72)Inventor : FUJINO TAKASHI
WATANUKI YUSUKE
ROKKAKU TAKAHIRO
KOJIMA TETSUO
UEDA SADAO
NAKANO MINORU

(54) NONAQUEOUS ELECTROLYTE FOR SECONDARY BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To enhance battery characteristics such as charging/discharging cycle characteristic, a low temperature discharge characteristic, or a storage characteristic by adding a silicon series anti-foaming agent represented by a specific formula to an electrolyte having concentration of the specified weight percent.



SOLUTION: A silicone series anti-foaming agent represented by the formula [in the formula, R represents an organic group or a hydrogen atom, which may be the same or different] is used as a silicone series anti-foaming agent to be added. As the organic group, an alkyl group and an aryl group are listed, and the alkyl group having a low molecular weight is used to increase the conductivity of an electrolyte. As the example of the alkyl group, a methyl group and an ethyl group are listed, and as the example of the aryl group, a phenyl group is listed. The concentration of the anti-foaming agent in the nonaqueous electrolyte is preferable to be 10 ppm to 10 wt.% since too low concentration does not show sufficient effect and too high concentration tends to decrease the capacity of a battery.

LEGAL STATUS
[Date of request for examination]
[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁（JP）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平11－185804

(43)公開日 平成11年(1999)7月9日

(51)Int.Cl.⁶	識別記号	F I	
H01M 10/40		H01M 10/40	A

審査請求 未請求 請求項の数3 FD（全6頁）

(21)出願番号 特願平9－363895

(22)出願日 平成9年(1997)12月18日

(71)出願人 000238953
富山薬品工業株式会社
東京都中央区日本橋本町一丁目2番6号

(72)発明者 藤野 高志
埼玉県富士見市水谷東3－11－1 富山薬品工業株式会社志木工場内

(72)発明者 綿貫 祐介
埼玉県富士見市水谷東3－11－1 富山薬品工業株式会社志木工場内

(72)発明者 六角 睦広
埼玉県富士見市水谷東3－11－1 富山薬品工業株式会社志木工場内

(74)代理人 弁理士 佐藤 良博

最終頁に続く

(54)【発明の名称】 二次電池用非水電解液

(57)【要約】

【構成】 非水溶媒と、電解質としてリチウム化合物を含む二次電池用非水電解液に、シリコーン系消泡剤を添加してなる。

【効果】 非水溶媒を使用し、リチウム化合物を電解質として含有する二次電池用非水電解液における充放電の際の非水電解液の分解によるガス発生を抑制し、放電容量を向上させ、インピーダンス特性を改善できる

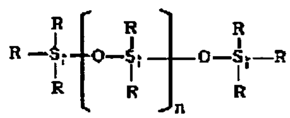
【特許請求の範囲】

【請求項1】 非水溶媒と、電解質としてリチウム化合物を含む二次電池用非水電解液において、シリコーン系消泡剤を添加してなることを特徴とする二次電池用非水電解液。

【請求項2】 シリコーン系消泡剤の二次電池用非水電解液中の濃度が、10ppm～10重量%であることを特徴とする、請求項1に記載の二次電池用非水電解液。

【請求項3】 シリコーン系消泡剤が、次の式1で表されるシリコーン系消泡剤であることを特徴とする、請求項1または2に記載の二次電池用非水電解液。

【式1】



但し、上記式中のRは、有機基もしくは水素原子であり、同一でも、異なっていてもよい。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リチウム化合物を電解質として含有する二次電池用非水電解液に関し、特に、負極と非水電解液中の溶媒との反応に起因する、低温放電特性の低下の防止、インピーダンス特性の改善を目的とした当該非水電解液の改良技術に関する。

【0002】

【従来の技術】近年、カメラ一体型VTR、携帯電話、ラップトップコンピュータ等の新しいポータブル電源として、特に、従来のニッケルーカドミニウム（Ni－Cd）二次電池や鉛二次電池に比べ軽量で高容量且つ高エネルギー密度のリチウム二次電池が注目されている。

【0003】従来より、リチウム二次電池の非水電解液の電解質としては、$LiPF_6$、$LiBF_4$等が、また、非水溶媒としては、炭酸プロピレン（PC）、炭酸エチレン（EC）、γ－ブチロラクトン（GBL）、炭酸ジメチル（DMC）、炭酸エチルメチル（MEC）、炭酸ジエチル（DEC）、酢酸エチル（EA）、プロピオン酸メチル（MPR）、1，2－ジメトキシエタン（DME）、2－メチルテトラヒドロフラン（2－MeTHF）等が用いられている。

【0004】しかしながら、負極活物質であるリチウムは反応性に富み、上記電解質と反応し、その反応生成物が電極表面に被膜となって付着し、その被膜が電池特性に大きく影響を与える。そこで、電池特性に悪影響を及ぼさないよう電解液組成が工夫されており、一般に、上記PCあるいはEC等の炭酸エステル類は、リチウムと反応してイオン伝導性を有する炭酸塩の被膜を生成する為、電池内部抵抗の増加等の電池特性に及ぼす悪影響は少なく、さらに、この被膜が負極表面の保護膜となり、

電池の保存特性等を良好にしているので、従来よりリチウム二次電池用非水電解液の主成分となっている。しかし、当該炭酸エステル類は、比較的融点が高く、また、当該PCあるいはEC等の環状のものは、粘性率が高く、さらに、上記DMCあるいはDEC等の直鎖状のものは、誘電率が低い為、上記GBLあるいはEA等のカルボン酸エステルと比較すると、電解液溶媒とした時の電解液の導電率が小さいという欠点がある。従って、高出力な二次電池として要求される充分な急速充電特性あるいは低温放電特性が得られなかった。さらに、炭酸エステル類は、二次電池の充電放電時あるいは高温下での保存中に、分解により炭酸ガスやオレフィンガスを生成する為、内圧が上昇し、電池が膨れるという問題があった。

【0005】

【発明が解決しようとする課題】本発明は、かかる従来技術の有する欠点を解消できる技術を提供することを目的としたものであって、特に、二次電池の充電放電サイクル特性、低温放電特性、保存特性等の電池特性を向上させることができる技術を提供することを目的とする。本発明の前記ならびにそのほかの目的と新規な特徴は、本明細書の記述および添付図面からもあきらかになるであろう。

【0006】

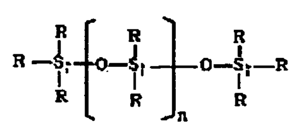
【課題を解決するための手段】本発明者らは、上述の目的を達成する為に、鋭意検討した結果、非水電解液二次電池の非水電解液へシリコーン系消泡剤を添加することにより、充放電における非水電解液の分解によるガス発生を抑制し、また、放電容量の向上、並びに、インピーダンス特性が改善できることを見出し、これに基づき、上述問題を解決する電解液を発明するに至った。すなわち、本発明は、非水溶媒と、電解質としてリチウム化合物を含む二次電池用非水電解液において、シリコーン系消泡剤を添加してなることを特徴とする二次電池用非水電解液に係るものである。

【0007】

【発明の実施の形態】以下、本発明を詳細に説明する。本発明において使用されるシリコーン系消泡剤の例としては、次の式1で表されるシリコーン系消泡剤が挙げられる。

【0008】

【式1】



【0009】但し、上記式中のRは、有機基もしくは水素原子であり、同一でも、異なっていてもよい。有機基であることが、本発明の目的から好ましい。有機基の例

としては、アルキル基、アリール基が挙げられる。当該アルキル基における炭素数には特に上限はないが、電解液の導電性を良好にするには、できるだけ低分子のアルキル基が好ましく、当該アルキル基の例には、メチル基、エチル基が挙げられる。アリール基の例としては、フェニル基が挙げられる。シリコーン系消泡剤として、上記のようなシリコーンオイルを溶剤に溶かした溶液型や各種添加剤を配合したもの等の二次製品的なものを使用できる。シリコーン系消泡剤は、市販のものを使用することができ、具体例としては、サンノプコ株式会社製ダッポーSN－357（以下、SN－357と称する。）、信越化学工業株式会社製KS603（以下、KS603と称する。）等が挙げられる。

【0010】シリコーン系消泡剤の非水電解液中での濃度は、低過ぎると添加した効果が充分でなく、高過ぎると電池容量が低下する傾向にあるので、10ppm～10重量%とすることが好ましい。

【0011】本発明において使用される非水溶媒としては特に限定されるものではなく、従来より二次電池用非水電解液において用いられているような溶媒を使用することができる。例えば、炭酸プロピレン（PC）、炭酸エチレン（EC）、炭酸ジメチル（DMC）、炭酸エチルメチル（MEC）、炭酸ジエチル（DEC）、γ－ブチロラクトン（GBL）、酢酸エチル（EA）、プロピオン酸メチル（MPR）、プロピオン酸エチル（EPR）、1，2－ジメトキシエタン（DME）、1，2－ジエトキシエタン（DEE）、2－メチルテトラヒドロフラン（2－MeTHF）、テトラヒドロフラン（THF）、スルホラン（SL）、メチルスルホラン（MeSL）等を使用することができ、これらは二種以上を混合してもよい。

【0012】本発明の二次電池用非水電解液においては、電解質としてリチウム化合物を使用する。これにより、本電解質はリチウム二次電池の電解液として特に有用となる。このようなリチウム化合物としては、従来のリチウム二次電池において用いられているものを使用することができる。例えば、$LiClO_4$、$LiAsF_6$、$LiPF_6$、$LiBF_4$、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$、$LiC(CF_3SO_2)_3$等を使用できる。尚、電解質であるリチウム化合物の二次電池用非水電解液中での濃度は、導電率の点から0．1～3．0mol／リットル、好ましくは0．3～2．0mol／リットルとするとよい。

【0013】本発明の二次電池用非水電解液は、例えば、非水溶媒を攪拌しながら、その中に電解質としてリチウム化合物を添加して溶解させ、シリコーン系消泡剤を添加して溶解させることにより製造することができる。

【0014】本発明の二次電池用非水電解液は、リチウム化合物を電解質とする、種々の構成の二次電池に適用

することができる。例えば、リチウム金属、リチウム合金またはリチウムをドープ・脱ドープすることができる材料からなる負極を有するリチウム二次電池に好ましく適用することができる。ここで、リチウム合金としては、リチウム－アルミニウム合金を例示することができる。また、リチウムをドープ・脱ドープすることができる材料としては、例えば、熱分解炭素類、コークス類（ピッチコークス、ニードルコークス、石油コークス等）、グラファイト類、有機高分子化合物焼成体（フェノール樹脂、フラン樹脂等を適当な温度で焼成し炭素化したもの）、炭素繊維、活性炭等の炭素材料等を使用することができる。

【0015】一方、正極は、充放電が可能な種々の材料から形成することができる。例えば、$LiCoO_2$、$LiNiO_2$、$LiMn_2O_4$、$LiMnO_2$などのLi_xMO_2（ここで、Mは一種以上の遷移金属であり、xは電池の充放電状態によって異なり、通常0．05≦x≦1．20である）で表される、リチウムと一種以上の遷移金属との複合酸化物や、FeS_2、TiS_2、V_2O_5、MoO_3、MoS_2などの遷移元素のカルコゲナイトあるいはポリアセチレン、ポリピロール等のポリマー等を使用することができる。

【0016】本発明の二次電池用非水電解液を使用した二次電池の形状については特に限定されることはなく、ボタン型、円筒型、角型、コイン型等の種々の形状にすることができる。

【0017】

【作用】本発明の二次電池用非水電解液において、非水電解液にシリコーン系消泡剤を含有させると、充電放電において、非水電解液の分解による炭酸ガス、オレフィンガス等の発生を抑制し、低温放電特性が向上され、インピーダンス特性を改善できる。

【0018】

【実施例】以下、本発明を実施例に基づいて更に説明する。

【0019】実施例1．当該実施例で用いた非水電解液二次電池につき、図1に基づいて説明する。図1に示すごとく、本例の非水電解液二次電池1は、正極2と負極3とセパレータ4と非水電解液5とボタン型電池容器6と正極側集電体7と負極側集電体8とガスケット9とを有してなる。上記正極2としては、$LiCoO_2$を正極活物質とする合剤をペレット状に加圧成形した成形品を使用した。また、負極3としては、コークスを負極活物質担体とした合剤をペレット状に加圧成形した成形品を使用した。非水電解液5には、炭酸エチレン（EC）と炭酸ジエチル（DEC）との混合溶媒（容量比2：3）に、$LiPF_6$からなる電解質を濃度1mol／リットルにて含有させ、さらに、シリコーン系消泡剤SN－357を0．05wt％含有してなる溶液を使用した。上記セパレータ4にはポリプロピレン製の不織布よりなる

セパレータを用いた。また、正極側集電体7はステンレス鋼により構成し、一方、負極側集電体8はニッケルエキスパンドメタルにより構成した。さらに、前記電池容器6はステンレス鋼より構成し、その正極缶と負極缶をポリプロピレンのガスケット9により固定した。以上のようにして作製した電池について、電池容量、低温放電時の電池容量、電池インピーダンスを調べた。尚、充電は定電流法とし、上限電圧を4．2V、定電流での電流密度を0．60（0．2C）mA／cm²に設定し、放電は、電流密度を0．60（0．2C）mA／cm²または3（1C）mA／cm²下定電流で行ない、終止電圧は2．7Vとした。通常充放電は20℃で実施した。低温放電時の電池容量は、通常充電した電池を－10℃に放置し、電流密度3（1C）mA／cm²で放電を実施し、通常放電した電池容量の比較から評価した。また、電池を温度90℃の環境下に100時間放置した後、電池を分解し、電解液を赤外分光光度計を使用して炭酸ガス濃度を測定して評価した。

【0020】実施例2．実施例1におけるシリコーン系消泡剤をKS603に変えた以外は、上記実施例1と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンス、電解液の炭酸ガス濃度を調べた。

【0021】実施例3．実施例1におけるシリコーン系消泡剤SN－357の含有量を0．1％に変えた以外は、実施例1と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンス、電解液の炭酸ガス濃度を調べた。

【0022】実施例4．実施例2におけるシリコーン系消泡剤KS603の含有量を0．1％とした以外は、実施例1と同様にしてボタン型電池を作製し、上述の同様＊の条件下で、電池容量、低温放電時の電池容量、インピーダンス、電解液の炭酸ガス濃度を調べた。

【0023】実施例5．上記実施例3における非水電解液を、炭酸エチレン（EC）と炭酸ジメチル（DMC）との混合溶媒（容量比1：1）とした以外は、実施例3と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンスを調べた。

【0024】実施例6．上記実施例4における非水電解液を、炭酸エチレン（EC）と炭酸ジメチル（DMC）との混合溶媒（容量比1：1）とした以外は、実施例4と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンスを調べた。

【0025】比較例1．実施例1においてシリコーン系消泡剤を添加しなかった以外は、実施例1と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンス、電解液の炭酸ガス濃度を調べた。

【0026】比較例2．実施例5において、シリコーン系消泡剤を添加しなかった以外は、実施例5と同様にしてボタン型電池を作製し、実施例1と同様の条件下で、電池容量、低温放電時の電池容量、インピーダンス、電解液の炭酸ガス濃度を調べた。

【0027】以上の結果を、表1、図2（A）及び図2（B）に示す。尚、図2（A）は、実施例3および実施例4と比較例1の低温放電後のインピーダンス曲線を示す。また、図2（B）は、実施例5および実施例6と比較例2の低温放電後のインピーダンス曲線を示す。

【0028】

【表1】

項目 / 例 No.	初期放電容量 (mAh)	低温放電時の電池容量 (mAh)	90℃、100時間放電後の電解液中の炭酸ガス濃度 (ppm)
実施例 1	2.81	1.32	750
実施例 2	2.83	1.34	470
実施例 3	2.86	1.48	650
実施例 4	2.83	1.33	540
実施例 5	2.77	1.39	―――
実施例 6	2.72	1.30	―――
比較例 1	2.58	1.12	1200
比較例 2	2.55	1.10	1120

【0029】表1に示すように、本発明のシリコーン系消泡剤を添加した電解液（実施例1～6）は、初期放電容量、低温放電時の電池容量の全てにおいて、当該シリコーン系消泡剤を加えていない電解液（比較例1．比較例2）に比較して、増加が見られ、効果があることが判る。図2（A）は、実施例3および実施例4と比較例1

の低温放電後のインピーダンス曲線を示すが、当該図2（A）に示すように、実施例3、実施例4とも比較例1に比べインピーダンスが下がり優れていることが判る。また、図2（B）は、実施例5および実施例6と比較例2の低温放電後のインピーダンス曲線を示すが、当該図2（B）に示すように、実施例5、実施例6とも比較例2に比べインピーダンスが下がり優れていることが判る。さらに、シリコーン系消泡剤を添加した電解液（実施例1～4）は、90℃、100時間放置後の炭酸ガス濃度において、当該シリコーン系消泡剤を加えていない電解液（比較例1、比較例2）に比較して、低下が見られ、効果があることが判る。

【0030】以上本発明者によってなされた発明を実施例にもとずき具体的に説明したが、本発明は上記実施例に限定されるものではなく、その要旨を逸脱しない範囲で種々変更可能であることはいうまでもない。例えば、上記実施例では、電池の形状はボタン型で説明を行なったが、これに限定されるものではなく、他の角型、円筒型、コイン型等であっても同様の効果を得ることが出来る。

【0031】

【発明の効果】本願において開示される発明のうち代表＊的なものによって得られる効果を簡単に説明すれば、下記のとおりである。すなわち、本発明によれば、二次電池用非水電解液において、シリコーン系消泡剤を添加することにより、その電解液を用いた二次電池の放電特性、低温放電特性、および分解ガスの抑制を向上させることができる。

【図面の簡単な説明】

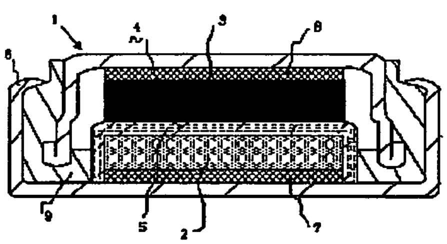
【図1】図1は、本発明の実施例に係る非水電解液二次電池の一例断面図である。

【図2】図2（A）および（B）は、それぞれ、本発明の作用効果を説明する低温放電後のインピーダンス曲線によるグラフである。

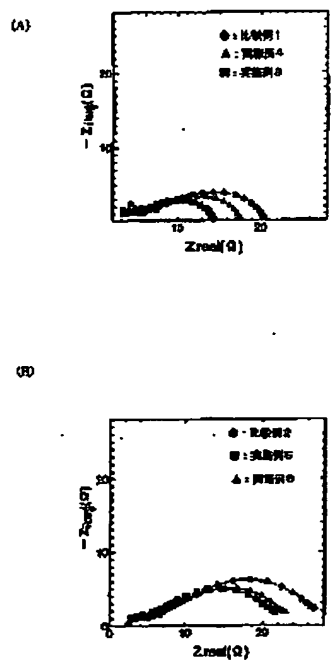
【符号の説明】

1…非水電解液二次電池
2…正極
3…負極
4…セパレータ
5…非水電解液
6…ボタン型電池容器
7…正極側集電体
8…負極側集電体
9…ガスケット

【図1】



【図2】



フロントページの続き

(72)発明者　小島　哲雄
埼玉県富士見市水谷東3－11－1　富山薬品工業株式会社志木工場内

(72)発明者　上田　定夫
埼玉県富士見市水谷東3－11－1　富山薬品工業株式会社志木工場内

(72)発明者　中野　稔
埼玉県富士見市水谷東3－11－1　富山薬品工業株式会社志木工場内

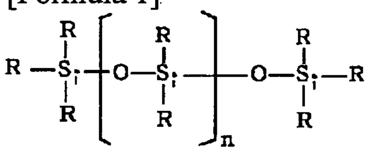
* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

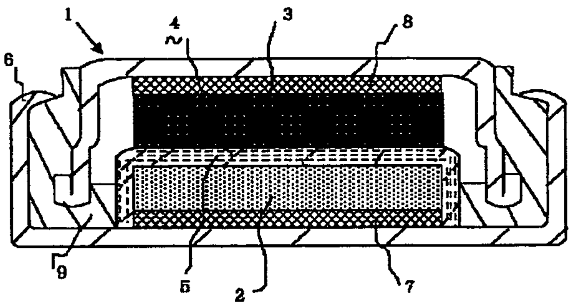
[Claim(s)]
[Claim 1] Nonaqueous electrolyte for rechargeable batteries which adds a silicone system defoaming agent and is characterized by the bird clapper in a non-aqueous solvent and the nonaqueous electrolyte for rechargeable batteries which contains a lithium compound as an electrolyte.
[Claim 2] Nonaqueous electrolyte for rechargeable batteries according to claim 1 to which concentration in the nonaqueous electrolyte for rechargeable batteries of a silicone system defoaming agent is characterized by being 10 ppm - 10 % of the weight.
[Claim 3] Nonaqueous electrolyte for rechargeable batteries according to claim 1 or 2 characterized by a silicone system defoaming agent being a silicone system defoaming agent expressed with the following formula 1.
[Formula 1]



However, R in the above-mentioned formula is an organic machine or a hydrogen atom, and even if the same, it may differ.

[Translation done.]

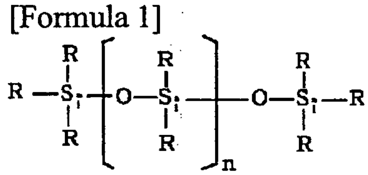
Drawing selection drawing 1



[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the improvement technology of the nonaqueous electrolyte concerned aiming at prevention of a fall of the low-temperature electric discharge property which originates in the reaction of a negative electrode and the solvent in nonaqueous electrolyte especially, and the improvement of an impedance characteristic about the nonaqueous electrolyte for rechargeable batteries which contains a lithium compound as an electrolyte.
[0002]
[Description of the Prior Art] In recent years, as new portable power supplies, such as a camcorder/movie, a cellular phone, and a laptop computer, especially, compared with a conventional nickel cadmium NIUMU (nickel-Cd) rechargeable battery and a conventional lead rechargeable battery, it is lightweight, and the lithium secondary battery of high capacity and high-energy density attracts attention.
[0003] Conventionally, LiPF6 and LiBF4 grade are used as an electrolyte of the nonaqueous electrolyte of a lithium secondary battery, and a propylene carbonate (PC), an ethylene carbonate (EC), gamma-butyrolactone (GBL), a dimethyl carbonate (DMC), an ethyl-carbonate methyl (MEC), diethyl carbonate (DEC), ethyl acetate (EA), a methyl propionate (MPR), 1, 2-dimethoxyethane (DME), 2-methyl tetrahydrofuran (2-MeTHF), etc. are used as a non-aqueous solvent.
[0004] However, the lithium which is a negative-electrode active material is rich in reactivity, and reacts with the above-mentioned electrolyte, the resultant serves as a coat, and adheres to an electrode front face, and the coat affects a cell property greatly. Then, in order to generate the coat of the carbonate which electrolytic-solution composition is devised so that it may not have a bad influence on a cell property, carbonates, such as Above PC and EC, generally react with a lithium, and has ion conductivity, there are few bad influences which it has on cell properties, such as an increase in cell internal resistance, and since this coat turns into a protective coat on the front face of a negative electrode and the preservation property of a cell etc. is made good, it is the principal component of the nonaqueous electrolyte for lithium secondary batteries conventionally further. However, what has the PC concerned or EC high the melting point and annular etc. has [the carbonates concerned] comparatively high coefficient of viscosity, and the thing of the shape of a straight chain, such as Above DMC and DEC, has further the fault that the conductivity of the electrolytic solution when a dielectric constant considers as an electrolytic-solution solvent as compared with carboxylates, such as Above GBL or EA, for a low reason is small. Therefore, sufficient boosting-charge property or the low-temperature electric discharge property demanded as a high power rechargeable battery was not acquired. Furthermore, in order for carbonates to generate carbon dioxide gas and olefin gas by decomposition, internal pressure rose and the problem that a cell blistered was during the preservation under the time of charge electric discharge of a rechargeable battery, or an elevated temperature.

[0005]
[Problem(s) to be Solved by the Invention] this invention aims at offering the technology which can raise especially the cell property which are the charge electric discharge cycle property of a rechargeable battery, a low-temperature electric discharge property, a preservation property, etc. for the purpose of offering the technology which can cancel the fault which this conventional technology has The other purposes and the new feature will become clear also from description and the accompanying drawing of this specification at the aforementioned row of this invention.
[0006]
[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of inquiring wholeheartedly, by adding a silicone system defoaming agent to the nonaqueous electrolyte of a nonaqueous electrolyte rechargeable battery, this invention persons find out that the generation of gas by decomposition of the nonaqueous electrolyte in charge and discharge is suppressed, and the improvement in service capacity and an impedance characteristic can improve, and came to invent the electrolytic solution which solves the above-mentioned problem based on this. That is, this invention relates to the nonaqueous electrolyte for rechargeable batteries which adds a silicone system defoaming agent and is characterized by the bird clapper in a non-aqueous solvent and the nonaqueous electrolyte for rechargeable batteries which contains a lithium compound as an electrolyte.
[0007]
[Embodiments of the Invention] Hereafter, this invention is explained in detail. As an example of the silicone system defoaming agent used in this invention, the silicone system defoaming agent expressed with the following formula 1 is mentioned.
[0008]
[Formula 1]


[0009] However, R in the above-mentioned formula is an organic machine or a hydrogen atom, and even if the same, it may differ. It is desirable from the purpose of this invention that it is an organic machine. An alkyl group and an aryl group are mentioned as an example of an organic machine. Although there is especially no upper limit in the carbon number in the alkyl group concerned, in order to make conductivity of the electrolytic solution good, a low-molecular alkyl group is desirable as much as possible, and a methyl group and an ethyl group are mentioned as the example of the alkyl group concerned. A phenyl group is mentioned as an example of an aryl group. Things like a secondary product, such as what blended the solution type which melted the above silicone oils to the solvent, and various additives as a silicone system defoaming agent, can be used. a silicone system defoaming agent -- a commercial thing -- it can be used -- as an example -- the Sannopuko, Inc. make -- DAPPO-SN-357 (SN-357 are called hereafter.), KS603 (KS603 is called hereafter.) by Shin-Etsu Chemical Co., Ltd., etc. are mentioned
[0010] the concentration in the inside of the nonaqueous electrolyte of a silicone system defoaming agent was added when too low -- an effect is not enough, and since it is in the inclination for cell capacity to fall when too high, it is desirable to consider as 10 ppm - 10 % of the weight
[0011] It is not limited especially as a non-aqueous solvent used in this invention, and a solvent which is conventionally used in the nonaqueous electrolyte for rechargeable batteries can be used. For example, a propylene carbonate (PC), an ethylene carbonate (EC), a dimethyl carbonate (DMC), An ethyl-carbonate methyl (MEC), diethyl carbonate (DEC), gamma-butyrolactone (GBL), Ethyl acetate (EA), a methyl propionate (MPR), an ethyl propionate (EPR), 1, 2-dimethoxyethane (DME), 1, 2-diethoxy ethane (DEE), 2-methyl tetrahydrofuran (2-MeTHF), a tetrahydrofuran (THF), a sulfolane

(SL), a methyl sulfolane (MeSL), etc. can be used, and these may mix two or more sorts.
[0012] In the nonaqueous electrolyte for rechargeable batteries of this invention, a lithium compound is used as an electrolyte. Thereby, this electrolyte becomes useful especially as the electrolytic solution of a lithium secondary battery. What is used in the conventional lithium secondary battery as such a lithium compound can be used. LiClO4, LiAsF6, LiPF6, LiBF4, and LiCF3 -- SO3, LiN (CF3SO2)2, and LiC(CF3SO2)3 grade can be used [for example,] In addition, as for the concentration in the inside of the nonaqueous electrolyte for rechargeable batteries of the lithium compound which is an electrolyte, it is good to make 0.1-3.0 mols /desirable in 0.3-2.0 mols/l. l. from the point of conductivity.
[0013] The nonaqueous electrolyte for rechargeable batteries of this invention can be manufactured by adding a lithium compound as an electrolyte, making it dissolve into it, adding a silicone system defoaming agent and making it dissolve, agitating a non-aqueous solvent.
[0014] The nonaqueous electrolyte for rechargeable batteries of this invention can apply a lithium compound to the rechargeable battery of the various composition used as an electrolyte. For example, it is preferably applicable to the lithium secondary battery which has the negative electrode which consists of material which can dope and ** dope a lithium metal, a lithium alloy, or a lithium. Here, a lithium aluminium alloy can be illustrated as a lithium alloy. Moreover, as a material which can dope and ** dope a lithium, carbon materials, such as pyrolytic carbons, corks (pitch coke, a needle coke, petroleum coke, etc.), graphite, an organic high-molecular-compound baking object (that which calcinated and carbonized phenol resin, the furan resin, etc. at suitable temperature), a carbon fiber, and activated carbon, etc. can be used, for example.
[0015] On the other hand, a positive electrode can be formed from the various material in which charge and discharge are possible. For example, LixMO(s)2 (here), such as LiCoO2, LiNiO2, LiMn2O4, and LiMnO2 M is the transition metals more than a kind, and x changes with charge-and-discharge states of a cell. 0.05<=x<=1.20 [usually,] -- it is -- the multiple oxide of the lithium and the transition metals more than a kind which are expressed -- Polymer, such as a cull scorch night of transition elements, such as FeS2, TiS2, V2O5, and MoO3, MoS2, or a polyacethylene, and polypyrrole, etc. can be used.
[0016] It is not limited especially about the configuration of the rechargeable battery which used the nonaqueous electrolyte for rechargeable batteries of this invention, and can be made various configurations, such as a button type, cylindrical, a square shape, and a coin type.
[0017]
[Function] In the nonaqueous electrolyte for rechargeable batteries of this invention, if nonaqueous electrolyte is made to contain a silicone system defoaming agent, in charge electric discharge, generating of the carbon dioxide gas by decomposition of nonaqueous electrolyte, olefin gas, etc. is suppressed, a low-temperature electric discharge property improves, and an impedance characteristic can be improved.
[0018]
[Example] Hereafter, this invention is further explained based on an example.
[0019] example 1. -- based on drawing 1 , it explains about the nonaqueous electrolyte rechargeable battery used in the example concerned As shown in drawing 1 , the nonaqueous electrolyte rechargeable battery 1 of this example has a positive electrode 2, a negative electrode 3, separator 4, nonaqueous electrolyte 5, the button type cell container 6, the positive-electrode side charge collector 7, the negative-electrode side charge collector 8, and a gasket 9, and becomes. The mold goods which carried out pressing of the mixture which makes LiCoO2 a positive active material to the shape of a pellet as the above-mentioned positive electrode 2 were used. Moreover, the mold goods which carried out pressing of the mixture which made corks negative-electrode active material support to the shape of a pellet as a negative electrode 3 were used. in nonaqueous electrolyte 5, the electrolyte which becomes the mixed solvent (capacity factor 2:3) of an ethylene carbonate (EC) and diethyl carbonate (DEC) from LiPF6 is contained by the concentration of one mol/l. -- making -- further --

silicone system defoaming-agent SN-357 -- 0.05wt(s)% -- the solution which it comes to contain was used The separator which consists of a nonwoven fabric made from polypropylene was used for the above-mentioned separator 4. Moreover, stainless steel constituted the positive-electrode side charge collector 7, and, on the other hand, it constituted the negative-electrode side charge collector 8 by the nickel expanded metal. Furthermore, the aforementioned cell container 6 was constituted from stainless steel, and fixed the positive-electrode can and negative-electrode can with the gasket 9 of polypropylene. About the cell produced as mentioned above, cell capacity, the cell capacity at the time of low-temperature electric discharge, and the cell impedance were investigated. In addition, charge was made into the galvanostatic process, the current density in 4.2V and a constant current was set as 0.60 (0.2C) mA/cm2 for upper limit voltage, electric discharge performed current density by 0.60 (0.2C) mA/cm2 or the bottom constant current of 3 (1C) mA/cm2, and final voltage was set to 2.7V. Usually, charge and discharge were carried out at 20 degrees C. The cell capacity at the time of low-temperature electric discharge was evaluated from comparison of the cell capacity which left the usually charged cell at -10 degrees C, discharged by current density 3 (1C) mA/cm2, and usually discharged. Moreover, after leaving a cell under environment with a temperature of 90 degrees C for 100 hours, the cell was disassembled, using the infrared spectrophotometer, carbon-dioxide-gas concentration was measured and the electrolytic solution was evaluated.
[0020] Except having changed the silicone system defoaming agent in the example 2. example 1 into KS603, the button type cell was produced like the above-mentioned example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0021] Except having changed the content of silicone system defoaming-agent SN-357 in the example 3. example 1 to 0.1%, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0022] Except having made the content of the silicone system defoaming agent KS603 in the example 4. example 2 into 0.1%, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same above-mentioned conditions.
[0023] Except having made the nonaqueous electrolyte in the example 5. above-mentioned example 3 into the mixed solvent (capacity factor 1:1) of an ethylene carbonate (EC) and a dimethyl carbonate (DMC), the button type cell was produced like the example 3, and cell capacity, the cell capacity at the time of low-temperature electric discharge, and the impedance were investigated under the same conditions as an example 1.
[0024] Except having made the nonaqueous electrolyte in the example 6. above-mentioned example 4 into the mixed solvent (capacity factor 1:1) of an ethylene carbonate (EC) and a dimethyl carbonate (DMC), the button type cell was produced like the example 4, and cell capacity, the cell capacity at the time of low-temperature electric discharge, and the impedance were investigated under the same conditions as an example 1.
[0025] Except having not added a silicone system defoaming agent in the example of comparison 1. example 1, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0026] In the example of comparison 2. example 5, except having not added a silicone system defoaming agent, the button type cell was produced like the example 5, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas

concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0027] The above result is shown in Table 1, drawing 2 (A), and drawing 2 (B). In addition, drawing 2 (A) shows the impedance curve after low-temperature electric discharge of an example 3 and an example 4, and the example 1 of comparison. Moreover, drawing 2 (B) shows the impedance curve after low-temperature electric discharge of an example 5 and an example 6, and the example 2 of comparison.
[0028]
[Table 1]

項目 / 例 No.	初期放電容量 (mAh)	低温放電時の電池容量 (mAh)	90℃、100時間放電後の電解液中の炭酸ガス濃度 (ppm)
実施例 1	2.81	1.32	750
実施例 2	2.83	1.34	470
実施例 3	2.86	1.48	650
実施例 4	2.83	1.33	540
実施例 5	2.77	1.39	————
実施例 6	2.72	1.30	————
比較例 1	2.58	1.12	1200
比較例 2	2.55	1.10	1120

[0029] As shown in Table 1, it turns out that an increase is seen as compared with the electrolytic solution (the example 1 of comparison, example 2 of comparison) which is not adding the silicone system defoaming agent concerned, and the electrolytic solution (examples 1-6) which added the silicone system defoaming agent of this invention is effective in initial service capacity and all the cell capacity at the time of low-temperature electric discharge. Although the impedance curve after low-temperature electric discharge of an example 3 and an example 4, and the example 1 of comparison is shown, as shown in the drawing 2 (A) concerned, as for drawing 2 (A), an example 3 and an example 4 are known by an impedance falling and excelling compared with the example 1 of comparison. Moreover, although the impedance curve after low-temperature electric discharge of an example 5 and an example 6, and the example 2 of comparison is shown, as shown in the drawing 2 (B) concerned, as for drawing 2 (B), an example 5 and an example 6 are known by an impedance falling and excelling compared with the example 2 of comparison. Furthermore, it turns out that a fall is seen as compared with the electrolytic solution (the example 1 of comparison, example 2 of comparison) which is not adding the silicone system defoaming agent concerned, and the electrolytic solution (examples 1-4) which added the silicone system defoaming agent is effective in the carbon-dioxide-gas concentration after 90 degrees C and 100-hour neglect.
[0030] invention made by this invention person above -- an example -- a basis -- **** -- although explained concretely, it cannot be overemphasized by this invention that it can change variously in the range which is not limited to the above-mentioned example and does not deviate from the summary For example, in the above-mentioned example, although the button type explained, the configuration of a cell is not limited to this, and even if they are other square shapes, cylindrical, a coin type, etc., it can acquire the same effect.
[0031]
[Effect of the Invention] It will be as follows if the effect acquired by the typical thing among

invention indicated in this application is explained briefly. That is, according to this invention, in the nonaqueous electrolyte for rechargeable batteries, suppression of the electric discharge property of the rechargeable battery using the electrolytic solution, a low-temperature electric discharge property, and cracked gas can be raised by adding a silicone system defoaming agent.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the improvement technology of the nonaqueous electrolyte concerned aiming at prevention of a fall of the low-temperature electric discharge property which originates in the reaction of a negative electrode and the solvent in nonaqueous electrolyte especially, and the improvement of an impedance characteristic about the nonaqueous electrolyte for rechargeable batteries which contains a lithium compound as an electrolyte.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In recent years, as new portable power supplies, such as a camcorder/movie, a cellular phone, and a laptop computer, especially, compared with a conventional nickel cadmium NIUMU (nickel-Cd) rechargeable battery and a conventional lead rechargeable battery, it is lightweight, and the lithium secondary battery of high capacity and high-energy density attracts attention.

[0003] From the former, it is an electrolyte of the nonaqueous electrolyte of a lithium secondary battery. $LiPF_6$ and the $LiBF_4$ grade are used for a propylene carbonate (PC), an ethylene carbonate (EC), gamma-butyrolactone (GBL), a dimethyl carbonate (DMC), an ethyl-carbonate methyl (MEC), diethyl carbonate (DEC), ethyl acetate (EA), a methyl propionate (MPR), 1, 2-dimethoxyethane (DME), 2-methyl tetrahydrofuran (2-MeTHF), etc. as a non-aqueous solvent again.

[0004] However, the lithium which is a negative-electrode active material is rich in reactivity, and reacts with the above-mentioned electrolyte, the resultant serves as a coat, and adheres to an electrode front face, and the coat affects a cell property greatly. Then, electrolytic-solution composition is devised so that it may not have a bad influence on a cell property, and generally carbonates, such as Above PC and EC, react with a lithium. In order to generate the coat of the carbonate which has ion conductivity, there are few bad influences which it has on cell properties, such as an increase in cell internal resistance, and since this coat turns into a protective coat on the front face of a negative electrode and the preservation property of a cell etc. is made good, it is the principal component of the nonaqueous electrolyte for lithium secondary batteries conventionally further. However, comparatively, what has the PC concerned or EC high the melting point and annular etc. has high coefficient of viscosity, and the carbonates concerned have the fault that its conductivity of the electrolytic solution when considering as an electrolytic-solution solvent as compared with carboxylates, such as Above GBL or EA, is still smaller since the thing of the shape of a straight chain, such as Above DMC and DEC, has a low dielectric constant. Therefore, sufficient boosting-charge property or the low-temperature electric discharge property demanded as a high power rechargeable battery was not acquired. Furthermore, in order for carbonates to generate carbon dioxide gas and olefin gas by decomposition, internal pressure rose and the problem that a cell blistered was during the preservation under the time of charge electric discharge of a rechargeable battery, or an elevated temperature.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] It will be as follows if the effect acquired by the typical thing among invention indicated in this application is explained briefly. That is, according to this invention, in the nonaqueous electrolyte for rechargeable batteries, suppression of the electric discharge property of the rechargeable battery using the electrolytic solution, a low-temperature electric discharge property, and cracked gas can be raised by adding a silicone system defoaming agent.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention aims at offering the technology which can raise especially the cell property which are the charge electric discharge cycle property of a rechargeable battery, a low-temperature electric discharge property, a preservation property, etc. for the purpose of offering the technology which can cancel the fault which this conventional technology has The other purposes and the new feature will become clear also from description and the accompanying drawing of this specification at the aforementioned row of this invention.

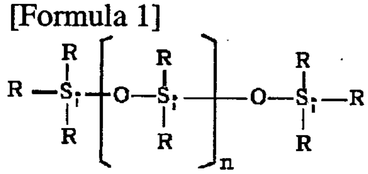
[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] In order to attain the above-mentioned purpose, as a result of inquiring wholeheartedly, by adding a silicone system defoaming agent to the nonaqueous electrolyte of a nonaqueous electrolyte rechargeable battery, this invention persons find out that the generation of gas by decomposition of the nonaqueous electrolyte in charge and discharge is suppressed, and the improvement in service capacity and an impedance characteristic can improve, and came to invent the electrolytic solution which solves the above-mentioned problem based on this. That is, this invention relates to the nonaqueous electrolyte for rechargeable batteries which adds a silicone system defoaming agent and is characterized by the bird clapper in a non-aqueous solvent and the nonaqueous electrolyte for rechargeable batteries which contains a lithium compound as an electrolyte.
[0007]
[Embodiments of the Invention] Hereafter, this invention is explained in detail. As an example of the silicone system defoaming agent used in this invention, the silicone system defoaming agent expressed with the following formula 1 is mentioned.
[0008]
[Formula 1]


[0009] However, R in the above-mentioned formula is an organic machine or a hydrogen atom, and even if the same, it may differ. It is desirable from the purpose of this invention that it is an organic machine. An alkyl group and an aryl group are mentioned as an example of an organic machine. Although there is especially no upper limit in the carbon number in the alkyl group concerned, in order to make conductivity of the electrolytic solution good, a low-molecular alkyl group is desirable as much as possible, and a methyl group and an ethyl group are mentioned as the example of the alkyl group concerned. A phenyl group is mentioned as an example of an aryl group. Things like a secondary product, such as what blended the solution type which melted the above silicone oils to the solvent, and various additives as a silicone system defoaming agent, can be used. a silicone system defoaming agent -- a commercial thing -- it can be used -- as an example -- the Sannopuko, Inc. make -- DAPPO-SN-357 (SN-357 are called hereafter.), KS603 (KS603 is called hereafter.) by Shin-Etsu Chemical Co., Ltd., etc. are mentioned
[0010] the concentration in the inside of the nonaqueous electrolyte of a silicone system defoaming agent was added when too low -- an effect is not enough, and since it is in the inclination for cell capacity to fall when too high, it is desirable to consider as 10 ppm - 10 % of the weight
[0011] It is not limited especially as a non-aqueous solvent used in this invention, and a solvent which is conventionally used in the nonaqueous electrolyte for rechargeable batteries can be used. For example, a propylene carbonate (PC), an ethylene carbonate (EC), a dimethyl carbonate (DMC), An ethyl-carbonate methyl (MEC), diethyl carbonate (DEC), gamma-butyrolactone (GBL), Ethyl acetate (EA), a methyl propionate (MPR), an ethyl propionate (EPR), 1, 2-dimethoxyethane (DME), 1, 2-diethoxy ethane (DEE), 2-methyl tetrahydrofuran (2-MeTHF), a tetrahydrofuran (THF), a sulfolane

---

OPERATION

[Function] In the nonaqueous electrolyte for rechargeable batteries of this invention, if nonaqueous electrolyte is made to contain a silicone system defoaming agent, in charge electric discharge, generating of the carbon dioxide gas by decomposition of nonaqueous electrolyte, olefin gas, etc. is suppressed, a low-temperature electric discharge property improves, and an impedance characteristic can be improved.

[Translation done.]

EXAMPLE

[Example] Hereafter, this invention is further explained based on an example.
[0019] example 1. -- based on drawing 1 , it explains about the nonaqueous electrolyte rechargeable battery used in the example concerned As shown in drawing 1 , the nonaqueous electrolyte rechargeable battery 1 of this example has a positive electrode 2, a negative electrode 3, separator 4, nonaqueous electrolyte 5, the button type cell container 6, the positive-electrode side charge collector 7, the negative-electrode side charge collector 8, and a gasket 9, and becomes. The mold goods which carried out pressing of the mixture which makes LiCoO2 a positive active material to the shape of a pellet as the above-mentioned positive electrode 2 were used. Moreover, the mold goods which carried out pressing of the mixture which made corks negative-electrode active material support to the shape of a pellet as a negative electrode 3 were used. in nonaqueous electrolyte 5, the electrolyte which becomes the mixed solvent (capacity factor 2:3) of an ethylene carbonate (EC) and diethyl carbonate (DEC) from LiPF6 is contained by the concentration of one mol/l. -- making -- further -- silicone system defoaming-agent SN-357 -- 0.05wt(s)% -- the solution which it comes to contain was used The separator which consists of a nonwoven fabric made from polypropylene was used for the above-mentioned separator 4. Moreover, stainless steel constituted the positive-electrode side charge collector 7, and, on the other hand, it constituted the negative-electrode side charge collector 8 by the nickel expanded metal. Furthermore, the aforementioned cell container 6 was constituted from stainless steel, and fixed the positive-electrode can and negative-electrode can with the gasket 9 of polypropylene. About the cell produced as mentioned above, cell capacity, the cell capacity at the time of low-temperature electric discharge, and the cell impedance were investigated. In addition, charge was made into the galvanostatic process, the current density in 4.2V and a constant current was set as 0.60 (0.2C) mA/cm2 for upper limit voltage, electric discharge performed current density by 0.60 (0.2C) mA/cm2 or the bottom constant current of 3 (1C) mA/cm2, and final voltage was set to 2.7V. Usually, charge and discharge were carried out at 20 degrees C. The cell capacity at the time of low-temperature electric discharge was evaluated from comparison of the cell capacity which left the usually charged cell at -10 degrees C, discharged by current density 3 (1C) mA/cm2, and usually discharged. Moreover, after leaving a cell under environment with a temperature of 90 degrees C for 100 hours, the cell was disassembled, using the infrared spectrophotometer, carbon-dioxide-gas concentration was measured and the electrolytic solution was evaluated.
[0020] Except having changed the silicone system defoaming agent in the example 2. example 1 into KS603, the button type cell was produced like the above-mentioned example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0021] Except having changed the content of silicone system defoaming-agent SN-357 in the example 3. example 1 to 0.1%, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.
[0022] Except having made the content of the silicone system defoaming agent KS603 in the example 4. example 2 into 0.1%, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-

gas concentration of the electrolytic solution were investigated under the same above-mentioned conditions.

[0023] Except having made the nonaqueous electrolyte in the example 5. above-mentioned example 3 into the mixed solvent (capacity factor 1:1) of an ethylene carbonate (EC) and a dimethyl carbonate (DMC), the button type cell was produced like the example 3, and cell capacity, the cell capacity at the time of low-temperature electric discharge, and the impedance were investigated under the same conditions as an example 1.

[0024] Except having made the nonaqueous electrolyte in the example 6. above-mentioned example 4 into the mixed solvent (capacity factor 1:1) of an ethylene carbonate (EC) and a dimethyl carbonate (DMC), the button type cell was produced like the example 4, and cell capacity, the cell capacity at the time of low-temperature electric discharge, and the impedance were investigated under the same conditions as an example 1.

[0025] Except having not added a silicone system defoaming agent in the example of comparison 1. example 1, the button type cell was produced like the example 1, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.

[0026] In the example of comparison 2. example 5, except having not added a silicone system defoaming agent, the button type cell was produced like the example 5, and cell capacity, the cell capacity at the time of low-temperature electric discharge, an impedance, and the carbon-dioxide-gas concentration of the electrolytic solution were investigated under the same conditions as an example 1.

[0027] The above result is shown in Table 1, drawing 2 (A), and drawing 2 (B). In addition, drawing 2 (A) shows the impedance curve after low-temperature electric discharge of an example 3 and an example 4, and the example 1 of comparison. Moreover, drawing 2 (B) shows the impedance curve after low-temperature electric discharge of an example 5 and an example 6, and the example 2 of comparison.

[0028]

[Table 1]

項目 / 例 No.	初期放電容量 (mAh)	低温放電時の電池容量 (mAh)	90℃、100時間放電後の電解液中の炭酸ガス濃度 (ppm)
実施例 1	2. 8 1	1. 3 2	7 5 0
実施例 2	2. 8 3	1. 3 4	4 7 0
実施例 3	2. 8 6	1. 4 8	6 5 0
実施例 4	2. 8 3	1. 3 3	5 4 0
実施例 5	2. 7 7	1. 3 9	―――
実施例 6	2. 7 2	1. 3 0	―――
比較例 1	2. 5 8	1. 1 2	1 2 0 0
比較例 2	2. 5 5	1. 1 0	1 1 2 0

[0029] As shown in Table 1, it turns out that an increase is seen as compared with the electrolytic solution (the example 1 of comparison, example 2 of comparison) which is not adding the silicone system defoaming agent concerned, and the electrolytic solution (examples 1-6) which added the silicone system defoaming agent of this invention is effective in initial service capacity and all the cell capacity at the time of low-temperature electric discharge. Although the impedance curve after low-temperature electric discharge of an example 3 and an example 4, and the example 1 of comparison is shown, as shown in the drawing 2 (A) concerned, as for drawing 2 (A), an example 3

and an example 4 are known by an impedance falling and excelling compared with the example 1 of comparison. Moreover, although the impedance curve after low-temperature electric discharge of an example 5 and an example 6, and the example 2 of comparison is shown, as shown in the drawing 2 (B) concerned, as for drawing 2 (B), an example 5 and an example 6 are known by an impedance falling and excelling compared with the example 2 of comparison. Furthermore, it turns out that a fall is seen as compared with the electrolytic solution (the example 1 of comparison, example 2 of comparison) which is not adding the silicone system defoaming agent concerned, and the electrolytic solution (examples 1-4) which added the silicone system defoaming agent is effective in the carbon-dioxide-gas concentration after 90 degrees C and 100-hour neglect.

[0030] invention made by this invention person above -- an example -- a basis -- **** -- although explained concretely, it cannot be overemphasized by this invention that it can change variously in the range which is not limited to the above-mentioned example and does not deviate from the summary For example, in the above-mentioned example, although the button type explained, the configuration of a cell is not limited to this, and even if they are other square shapes, cylindrical, a coin type, etc., it can acquire the same effect.

[Translation done.]

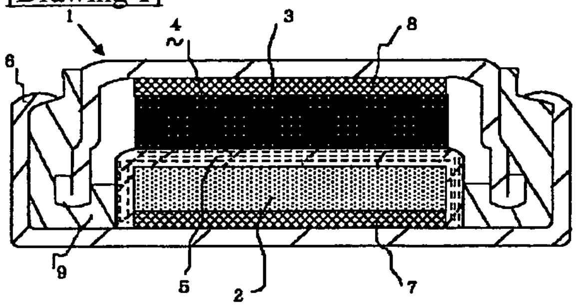
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is an example cross section of the nonaqueous electrolyte rechargeable battery concerning the example of this invention.
[Drawing 2] Drawing 2 (A) and (B) are graphs with the impedance curve after the low-temperature electric discharge explaining the operation effect of this invention, respectively.
[Description of Notations]
1 -- Nonaqueous electrolyte rechargeable battery
2 -- Positive electrode
3 -- Negative electrode
4 -- Separator
5 -- Nonaqueous electrolyte
6 -- Button type cell container
7 -- Positive-electrode side charge collector
8 -- Negative-electrode side charge collector
9 -- Gasket

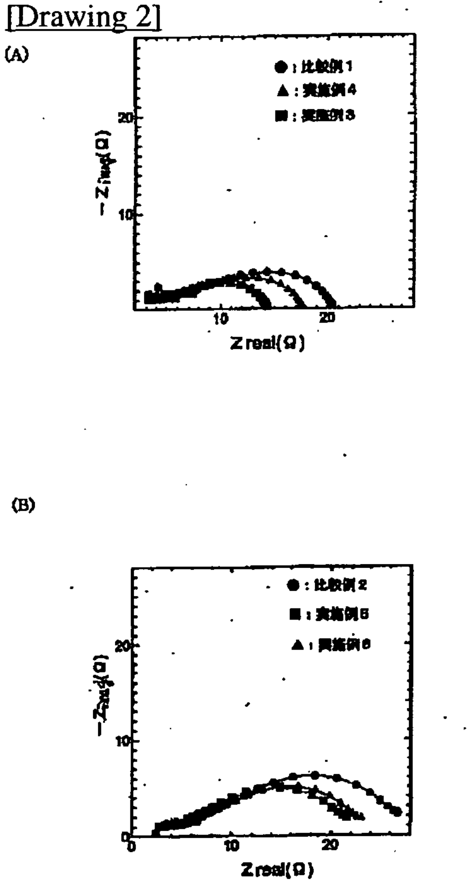
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]